Stainless steel corrosion under anoxic, highly saline and elevated temperature conditions

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Abstract. Several countries consider hosting a deep geological repository for high-level nuclear waste (HLW) in salt rock. In the unexpected case of solution access to the emplacement caverns during the long-term evolution of such a repository, metallic containers will be exposed to highly saline brines. In this study, corrosion experiments under conditions expected to be representative of HLW disposal in salt rock have been performed with stainless steel, a material typically used to construct containers containing vitrified HLW.

Experiments were performed in closed vessels under anoxic and highly saline conditions at 90 °C. Polished stainless steel coupons were suspended in 5 mol L⁻¹ NaCl or 3.4 mol L⁻¹ MgCl₂ at their natural pH. At the end of the experiments (up to 294 d), vessels were cooled down to room temperature, pH and Eₖ were measured in situ, the ultra-centrifuged contacting brines were analyzed by (HR)ICP-MS (high-resolution inductively coupled plasma mass spectrometry) and the formed corrosion products were identified.

In all corrosion experiments, pHₘ and Eₖ hardly changed with exposure time, and the nature of the salt had no significant effect. The overall corrosion rates were low, and the quantities of dissolved metal ions revealed the formation of only sparingly soluble corrosion products. The formation of a passivation layer mostly made of Cr(III) (hydr)oxide was evidenced, but no localized surface attack could be detected. The coupon corroded in 5 mol L⁻¹ NaCl was embedded in resin and cross-cut for further analyses, using synchrotron-based techniques with a small beam footprint (X-Ray fluorescence (μXRF), X-Ray diffraction (μXRD), and X-ray absorption near-edge structure (μXANES)). Element distribution maps revealed the presence of a very thin (< 1 µm) layer of corrosion products, with regions enriched either in Cr or in Fe and Ni. X-ray diffractograms identified the presence of spinel-type compounds (Fe₃O₄ and NiFe₂O₄) and Cr₂O₃, which was corroborated by recording μXANES at the Cr, Fe and Ni K-absorption edges. The additional presence of layered double hydroxides in addition to NiO and Ni(OH)₂ was also evidenced. Overall, results point to a corrosion layer having a duplex structure, with an inner layer mostly of chromium (hydr)oxides and an outer layer made of Fe- and Ni-based spinel compounds admixed with nickel (hydr)oxides.
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